



Visible Light-Driven high Photocatalytic Activity of Cu-Doped TiO₂ Nanoparticles Synthesized by Hydrothermal Method

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Abstract

TiO₂ and Cu-doped TiO₂ nanoparticles (NPs) with totally extraordinary substance of Cu by exploitation hydrothermal method. The part immaculateness, morphology, molecule estimate, optical properties, and elemental composition of as-incorporated Cu-doped TiO₂ NPs were investigated by numerous systematic methods. The XRD designs unveiled Cu-doped TiO₂ NPs inside the part unadulterated anatase phase. The plane of (101) XRD and XPS results show the lucky doping of Cu²⁺ inside the TiO₂ lattice. The optical edges of Cu-doped TiO₂ demonstrated a transparent light absorption in visible region that assumes an essential part inside the photocatalytic action underneath characteristic daylight. Certain Cu²⁺ content shows least PL intensity that backings the decrease in recombination rate of charge species. In addition, to get a handle on photocatalytic action, we have tried Cu-doped TiO₂ for the degradation of Malachite Green (MG) under visible light. A large portion of 85% degradation was found for Cu-doped TiO₂ (1.71 wt.%) underneath daylight minimum of 180 min, severally, that is past that of TiO₂ (53%). Also, the degradation of the MG was affirmed by measurement of the chemical oxygen demand of the photodegraded solution. These outcomes demonstrates that the Cu-doped TiO₂ NPs are extremely productive for the photodegradation of the MG.



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Introduction

Environment-friendly visible light determined photocatalyst for wastewater treatment are right now an exciting zone of research. In view of extraordinary properties of TiO_2 like high stability, minimal effort, photoelectric, and security to every human and the environment. TiO_2 as a metal oxide semiconductor has been generally utilized in ecological control of contamination, transformation and vitality storage, sensors, photovoltaics and Li-ion batteries.¹⁻² As of late a lot of interest has been dedicated for the photocatalytic degradation of natural water containing poisons group that begins from textile or any pharmaceutical industry by semiconductor materials.² Textiles materials are bad for ecological system because of their far reaching use and potential for dangerous fragrant species, while pharmaceutical industry is conceivable to continue expanding utilization of the organic compound that has extreme unfriendly impacts on the environment.³⁻⁴

Industries like paper, material, and printing produces an outsized measure of nephrotoxic and non-biodegradable color effluents that goes into the surroundings. Overabundance utilization of different colors in the material business has prompted the contamination of surface water and groundwater.⁵⁻⁶ For mechanical application, anatase TiO_2 has been favoured over rutile and brookite because of its higher photocatalytic activity.⁷ The photocatalytic degradation of a color includes the development of electrons (e^-) and holes (h^+) on the surface of the catalyst, which acts as redox sources that produces oxidative species, bringing about the destruction of pollutants.⁸

Nowadays, entirely scientific community everywhere attracted towards photocatalysis. The globe has connected towards the heterogeneous photocatalysis, particularly for the photocatalytic degradation of hazardous natural contaminants like azo dyes⁹, drugs¹⁰ and natural pollutants¹¹. A band gap of 3.2 eV of Anatase TiO_2 corresponds to 387.45 nm. Thus, it is photocatalytic upon exposure to light having wavelength less than or equal to 387.45nm that spreads exclusively 3-5% of the sunlight radiation.¹²⁻¹³ Consequently, developing visible-light-active TiO_2 fundamentally based structures with expanded photoactivity is basic need for a

considerable measure of prudent use of sunlight. Dynamic photocatalytic materials with wavelengths inside the visible radiation vary square measure necessity for indoor applications.¹⁴

The most economical way to extend the photoresponse of TiO_2 into visible is doping or surface modification with transition metals¹⁵ like Cr^{3+} ¹⁶⁻¹⁷, Mn^{2+} ¹⁸, Fe^{3+} ¹⁹⁻²⁰, Co^{2+} ²¹, Ni^{2+} ²², Cu^{2+} ²³. Among these dopants, Cu^{2+} has been widely utilised for the doping, because the radius of Cu^{2+} (0.87 Å) is totally different from that of Ti^{4+} ion (0.74 Å)²⁴⁻²⁵. Cu generally as a Cu^{2+} ion in oxide and Ti exist as a Ti^{4+} ion in TiO_2 , along these lines it's trusted that doping of Cu in TiO_2 could give oxygen opportunities inside the lattice that should upgrade the superhydrophilicity and photocatalytic activity.

In 2011, Nishikiori *et al.*²⁶ detailed a sol-gel blend of Cu-doped TiO_2 and tried its movement beneath visible radiation for the decolourization of Methylene Blue (MB) and trichloroethylene. The Cu-doped TiO_2 demonstrated a respectable photocatalytic action beneath visible radiation light as a result of the progress of the TiO_2 valence band to Cu^{2+} impurity states. In 2013, Hudson *et al.*²⁷ distributed their work on the combination of Cu- TiO_2 photocatalyst ready by the sol-gel system. The brilliant degradation proficiency was found for Cu- TiO_2 NPs (> 95%) in 30 min underneath daylight illumination, in contrast with TiO_2 (< 40%) for the degradation of Methylene Blue dye.

In 2014, Janeczarek *et al.*²⁸ examined the amalgamation of Cu- TiO_2 clear skinny films utilizing the sol-gel dip-coating procedure. The vital rate of phenol and 4-chlorophenol mineralization was resolved underneath light illumination. The photoactivity of total organic carbon (TOC) which is the concentration of organic carbon diminishes within 3 hours of illumination ($\lambda > 420$ nm) was 53% and 45% individually.

In 2015, Pongwan *et al.*²⁹ distributed their work on Cu-doped TiO_2 NPs utilizing the adjusted sol-gel strategy. Great photocatalytic activity was seen under visible light illumination for the mineralization of oxalic acid and formic acid with respect to TiO_2 . The ideal amount of Cu doping was 2.0mol.% demonstrating the best execution of oxalic and formic

Table 1: Crystallite size calculated from XRD (D_{XRD}), TEM diameter (D_{TEM}), Lattice constant (a/b, c), X-ray density (ρ_x), Specific surface area (S_a/m^2g^{-1}), Unit cell volume ($V/\text{\AA}^3$) and Band gap (eV)

Sample	D_{XRD} (nm)	D_{TEM} (nm)	Lattice Constant ($\text{\AA}$)		ρ_x (g/cm ³)	S_a/m^2g^{-1}	$V/\text{\AA}^3$	Band gap (eV)
			a/b	c				
a	11.01	11	3.775	9.509	0.3914	139.35	135.5	3.18
b	10.08	10	3.783	9.513	0.3896	154	136.14	2.72
c	8.8	9	3.783	9.511	0.3897	174.95	136.11	2.48
d	7.76	8	3.78	9.501	0.8266	197.84	135.75	2.34

acid mineralization under light irradiation. In 2016, Bensouici *et al.*³⁰ Revealed a sol-gel dip coating blend of Cu doped TiO₂ thin films kept on the glass substrate and tried its activity for deterioration of MB under UV light. The incredible photocatalytic activity was watched for the TiO₂ thin film (92%) in 180 minutes, while just 16 % degradation was seen in 4.6 and 10% Cu doped TiO₂ films.

To the best of our insight, we report here to integrate Cu-doped TiO₂ NPs by a basic hydrothermal method utilizing Titanium (IV) tetraisopropoxide (TTIP) as a source. This arrangement course offers the tuning of the band gap of TiO₂ to the coveted level through the doping of Cu²⁺ NPs. The photocatalytic action of Cu-doped TiO₂ NPs under UV, visible and coordinate daylight is explored towards the degradation of Malachite Green (MG) as a model contaminant. Malachite Green is cationic dye it refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$.

There are no reports on the doping of Cu²⁺ in TiO₂ by hydrothermal method at 120 °C in 5 hours. The goal in this examination work is to grow exceedingly effective, visible light dynamic photocatalyst in view of nanotechnology for detoxification of MG.

Experimental

Materials

All chemicals used were of AR grade and used as received without any purification. Titanium (IV) tetraisopropoxide (TTIP) (98%), Copper nitrate (99%), Glacial acetic acid (99%) were purchased from Spectrochem Pvt. Ltd., S D Fine-Chem Ltd., Mumbai (India) and Pune Chemical Laboratory. Throughout the experiment ethanol (99.9%) and double distilled water were used.

Synthesis of Cu-doped TiO₂ NPs

Cu-doped TiO₂ nanoparticles were synthesized by the hydrothermal method. TTIP and glacial acetic acid were taken in stoichiometric amount to get a transparent solution. Then the stoichiometric amount of copper nitrate (1, 2 and 3 wt.%) dissolved in double distilled water (DDW) which was then added into the above solution to get transparent solution. Afterword, solution was moved to Teflon lined autoclave that was sealed and kept for heating for a period of 5 hours at 120 °C. Autoclave was permitted to cool down to room temperature after heating. Ethanol was used to wash the catalyst. The total mixture was dried at 60°C to get Cu-doped TiO₂ NPs and annealed at 350 °C for 2 hours.

Characterization of the Catalyst

The X-ray pattern of samples were recorded using (Rigaku miniflex 600) with Cu-K α ($\lambda = 1.5406\text{\AA}$) radiation in the 2θ range from 20-80°. The optical properties were recorded by UV-Visible -NIR Spectrophotometer (Model V-770, Jasco). Transmission electron microscope (Jeol 3010) and energy dispersive X-ray spectrometer (Joel JSM

Table 2: EDS Composition (wt.%) of TiO₂ and Cu-doped TiO₂ NPs Composition (wt.%)

Ti	O	Cu
56.34	43.66	0
65.80	33.32	0.88
61.39	37.09	1.52
56.12	42.17	1.71

5600) was used to determine the composition of the element. The PL spectra was used to study the recombination of electron hole pairs (Model F.P. 8200). X-ray photoelectron spectroscopy (XPS) was used to study the surface composition of the photocatalyst using (K-alpha Thermo VG scientific). Raman spectra were recorded in the spectral range 100-700 cm^{-1} using Raman spectrometer (Horiba Jobin Vyon, France).

Photocatalytic Activity of Cu-Doped TiO_2 Nanoparticles

The photodegradation efficiency of Cu-doped TiO_2 NPs were evaluated by the degradation of MG dye. The UV tubes were placed inside a circular box. The 50 ppm MG dye solution with 5 mg of photocatalyst in a glass jar was stirred magnetically. To ensure the adsorption-desorption equilibrium, the suspension was stirred 30 min magnetically dark at room temperature and then exposed to UV light. After a precise time intervals, aliquots were taken out from the suspension and centrifuged, to separate the catalyst. The solution was additionally used to

monitor the concentration of MG dye by recording the absorbance of the solution on a UV-visible spectrophotometer. Similar experiments were done for the degradation of MG dye in visible and direct sunlight under the same reaction conditions.

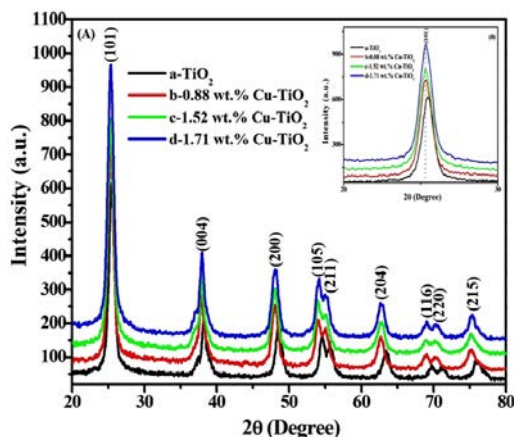


Fig. 1A: XRD Patterns of (a) TiO_2 , (b) 0.88, (c) 1.52 and (d) 1.71 wt.% Cu-Doped TiO_2 NPs and (B) Gaussian Fit

Table 3: Degradation of Malachite Green Dye under UV, Visible and Direct Sunlight using Cu-Doped TiO_2 NPs

Sample	Time of Irradiation in Minute					
	30	60	90	120	150	180
Under UV Light						
a	46.71	61.04	65.12	67.34	72	77.58
b	33.53	44.66	50.02	53.18	58.08	62.13
c	22.37	31.19	36.78	41.26	45.38	49.15
d	13.32	18.57	21.41	22.22	23.24	29.1
Under Visible Light						
a	21.83	30.12	36.46	42.86	46	49.66
b	28.67	35.31	43.41	48.32	53.23	57.58
c	36.7	44.02	51.74	58.29	64.08	69.87
d	46.32	54	62.1	66.16	71.84	78.32
Under Direct Sunlight						
a	25.33	33.62	39.96	46.36	49.5	53.16
b	27.22	38.18	43.75	50.49	54.41	59.88
c	36.81	45.67	53.41	59.65	63.17	69.88
d	48.72	60.32	67.86	72.48	77.5	85.1

Results and Discussion

The XRD patterns of TiO_2 and Cu-doped TiO_2 NPs is shown in (Fig. 1A) and the diffraction peak matches with the standard JCPDS card no. 21-1272. The main peak (101) Cu-doped TiO_2 had been found to be shifted to left side from 25.50° to 25.26° (Fig. 1B inset). The explanation for addition may be owing to the substitution of the six-coordinate Cu2p ions into the six-coordinate Ti4p D2d sites because the radius of Cu2p ion (ionic radius $0.87 \text{ \AA}$) is larger than the Ti4p ion (ionic radius $0.74 \text{ \AA}$). This was confirmed by XPS estimations later.³¹ It is because of doping

of Cu-doped TiO_2 , which confirms pure crystalline phase was developed throughout the synthesis. This was confirmed by XPS measurements mentioned later. The crystallite size, X-ray density, and specific surface area of the synthesized TiO_2 and Cu-doped TiO_2 NPs were estimated as per using the formula reported in the literature and our previous work²² and the calculated values are given in Table 1. The crystallite size of Cu-doped TiO_2 nanoparticles were smaller than those of TiO_2 nanoparticles. It has been seen that as the dopant concentration increases, the crystallite size reduces. This reduction

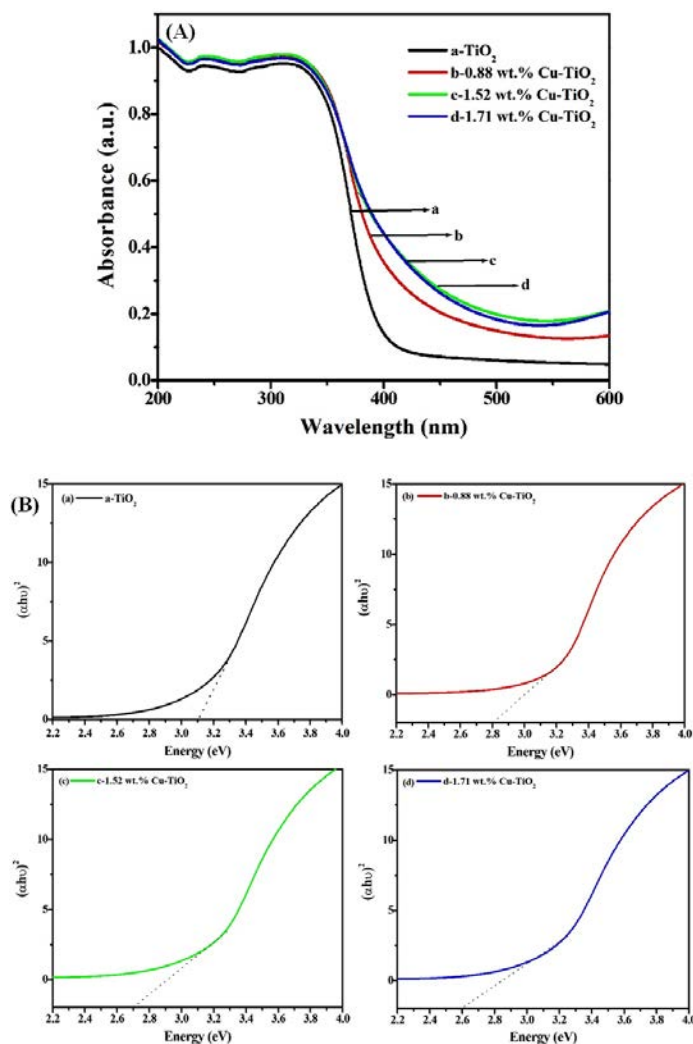


Fig. 2: (A) Optical Absorbance Spectra of (a) TiO_2 , (b) 0.88, (c) 1.52, (d) 1.71 and (B) Determination of Band Gap by Plotting $(\alpha h\nu)^2$ Versus Energy (eV) for (a) TiO_2 , (b) 0.88, (c) 1.52 and (d) 1.71 wt.% Cu-Doped TiO_2 NPs

in crystallite size are often altered and corrected to the rise in structural defects that makes particle bigger. The ionic radius of Cu^{2+} ion (0.87 Å) is totally different from that of Ti^{4+} ion (0.74 Å) that results to interchange some portion of Ti^{4+} ions by Cu^{2+} ions within the TiO_2 lattice.³²⁻³³ The right substitution of doping Cu^{2+} with associate oxidation state of lower in the TiO_2 host lattice generates a charge-correct ion vacancy and reduces the free electron concentration.

The absorption spectra of TiO_2 and Cu-doped TiO_2 NPs are shown in Fig. 2A. The absorption spectra of samples show band edge at 387, 453, 500, 530 nm for TiO_2 , 0.88, 1.52 and 1.71 wt.% Cu-doped TiO_2 NPs. This means that Copper-doping contributed to the band gap reduction. With rise in copper content band gap energy values of catalyst decreases and also the calculated band gap values are shown in Table 1. The longer wavelength absorption can be allotted to the formation of impurity levels among the lattice of TiO_2 .³⁴ The concentration of Cu^{2+} dopant ions within the host lattice of TiO_2 makes oxygen vacancies due to the charge compensation

impact and this could shift the optical absorption of Cu-doped TiO_2 nanoparticles extended within the visible light region.³⁵

Fig. 3A a-b is that the TEM micrographs and SAED pattern showing TiO_2 NPs, whereas that of Fig. 3A c-d shows Cu-doped TiO_2 (1.71 wt.%) NPs. The Cu-doped TiO_2 particle size obtained from TEM within the range 8-10nm. TEM micrographs show the particles agglomerated and non-uniform shape and size. The obtained size of the particle matches with the results of XRD. To study the presence of elements within the sample EDS analysis was used which is shown in Fig. 3B e, f, g and h. The existence of all elements like Ti, O and Cu in the sample shows by elemental map and therefore the corresponding values of Ti, O and Cu is shown in Table 2.

Fig. 4 shows the Raman spectra of TiO_2 and Cu-doped TiO_2 NPs. The highest peak seems at a 144, 200, 398, 517 and 640 cm^{-1} is recognized to Eg, B_{1g} , $\text{A}_{1g} + \text{B}_{1g}$ were found within the modes of all anatase TiO_2 samples. The Raman Eg peak of Cu-

Table 4: COD Values, with Respect to the Irradiation Time of an Aqueous Solution of Malachite Green using TiO_2 and Cu-Doped TiO_2 Catalysts

Sample	Time of Irradiation in Minute					
	30	60	90	120	150	180
Under UV Light						
a	292.02	213.5	191.14	178.97	153.44	122.86
b	364.25	303.26	273.89	256.57	229.72	207.52
c	425.41	377.07	346.44	321.89	299.31	278.65
d	475	446.23	430.67	426.23	420.64	388.53
Under Visible Light						
a	428.37	382.94	348.19	313.12	295.92	275.86
b	390.88	354.5	310.11	283.2	256.29	232.46
c	346.88	306.77	264.46	228.57	196.84	165.11
d	294.16	252.08	207.69	185.44	154.31	118.8
Under Direct Sunlight						
a	409.19	363.76	329.01	293.94	276.74	256.68
b	398.83	338.77	308.25	271.31	249.83	219.85
c	346.28	297.72	255.31	221.11	201.82	165.05
d	281.01	217.44	176.12	150.8	123.3	81.65

doped TiO_2 NPs exhibits a reduction within the peak intensity in addition as changes within the FWHM, ever-changing to 149 cm^{-1} likened to TiO_2 .

The quantitative investigation of electronic and chemical properties of the representative Cu-doped TiO_2 NPs was analysed by XPS as shown in Fig. 5. Fig. 5a shows the carbon impurities arising at 284.99 eV in the survey scan spectrum of XPS analysis. Fig. 5b shows the core level Ti2p spectra of Cu-doped TiO_2 sample. For TiO_2 , Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks are observed at 461.01 and 466.76 eV respectively. The splitting between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.75 eV, demonstrating a normal state of Ti^{4+} ion in the sample.³⁶⁻³⁷ Fig. 5c shows the XPS spectra of O1s configuration. The binding energies at 532.4 eV disclose the existence of surface hydroxyl groups and O1s electron binding energy arising from titanium lattice correspondingly. The tiny amendment within the binding energy of Ti atom clearly reveals the substitution of the few sites of the Ti^{4+} ion by Cu^{2+} ions.³⁸⁻³⁹ Fig. 5d shows the 1.71 wt.% Cu-doped TiO_2 sample, the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core-level peaks are located at 934.60 and 954.19 eV of Cu^{2+} ions respectively, indicating a traditional state of Cu^{2+} within the sample. The binding energy distinction

between the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core level is 19.5 eV respectively.

Fig. 6A,B shows the PL spectra of TiO_2 and Cu-doped TiO_2 NPs. It is a helpful technique to review the electronic structure and optical possessions of

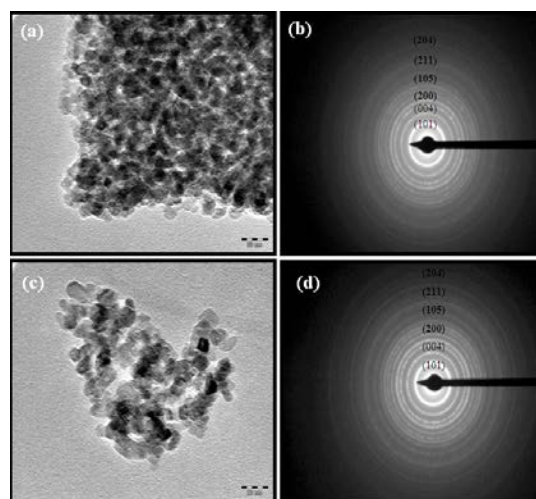


Fig. 3A: (a). TEM Image of TiO_2 , (b) SAED Pattern of TiO_2 , (c) 1.71 wt.% TEM Image and (d) SAED Pattern of Cu-Doped TiO_2

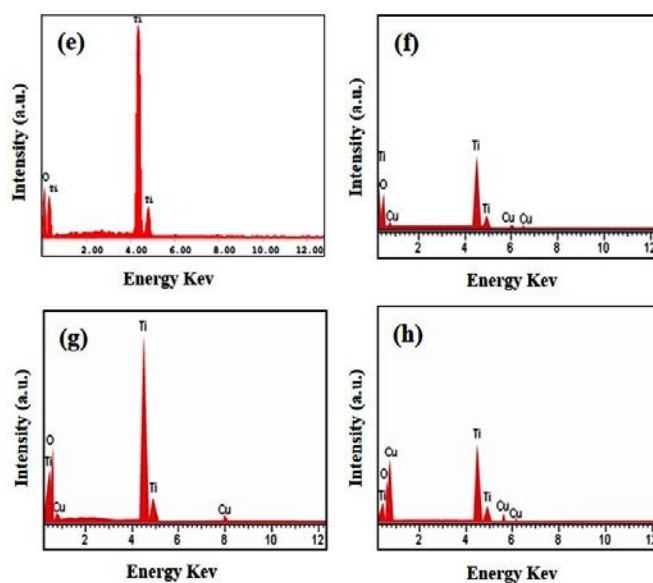


Fig. 3B: (e). EDS Spectrum of TiO_2 , (f) EDS Spectrum of 0.88, (g) 1.52 and (h) 1.71 wt.% Cu-Doped TiO_2 NPs

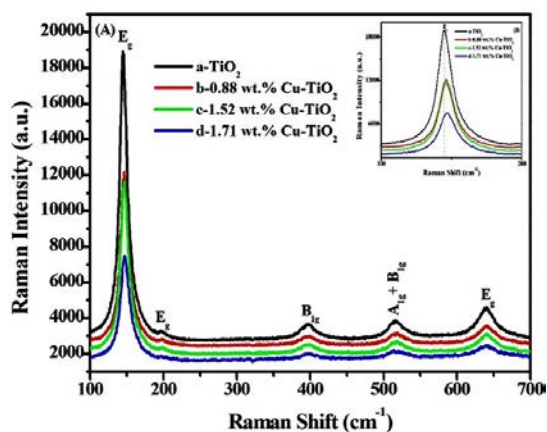


Fig. 4A: Raman Spectra of (a) TiO_2 , (b) 0.88, (c) 1.52 and (d) 1.71 wt.% Cu-Doped TiO_2 NPs (B) Guassian Fit

semiconductor materials. PL spectra is accustomed analyze the destiny of photo-generated e^- and h^+ during a semiconductor meanwhile PL emission results from the recombination of free charge carriers. The excitation wavelength 318 nm and

the emission peak detected at 411.13 nm for TiO_2 . The rise in Cu^{2+} concentration shifts the wavelength towards the upper region (469.72, 482.66 and 492.66 nm) with reducing peak strength for Cu-doped TiO_2 as shown in Fig. 6. The recombination rate of photogenerated charge transporters is reduced by surface imperfections. The oxygen opening and metal ions trap the energized e^- and h^+ separately. The energized e^- will move from the valence band to the new vitality levels presented by doping therefore will reduce the PL intensity.⁴⁰

TiO_2 and Cu-doped TiO_2 NPs samples were explored for the photodegradation of MG dye. In order to evaluate the photocatalytic activity of the Cu-doped TiO_2 for the degradation of dye under UV light, visible light and direct sunlight irradiations were investigated and summarized in Table 3. The absorption of the dye solution was measured using UV-visible spectrophotometer at its typical wavelength. The % degradation of each dye at different irradiated time intervals was calculated in step with the following equation.⁴¹

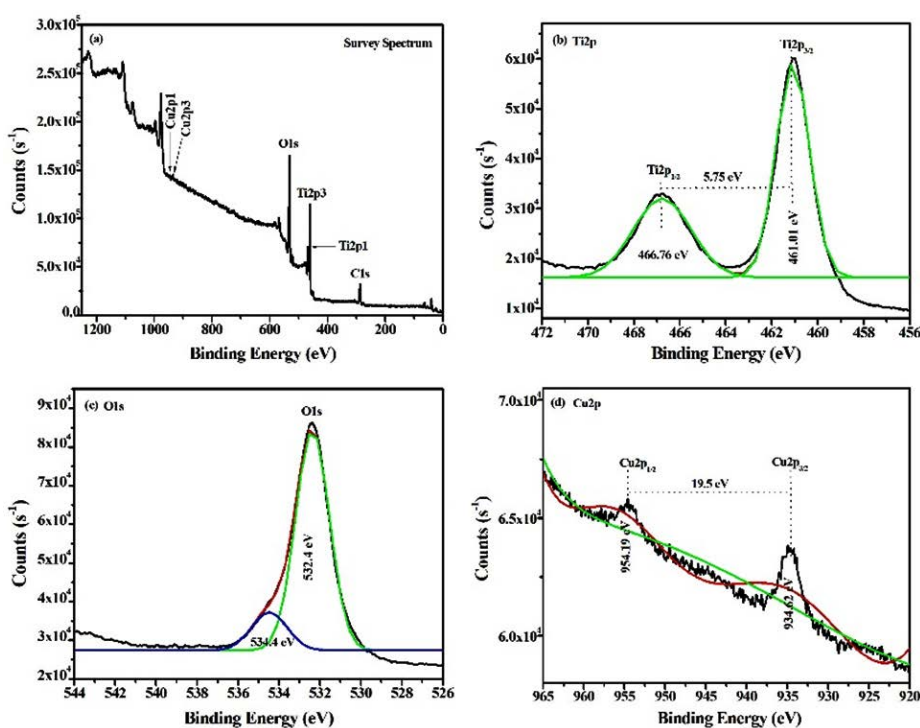


Fig. 5: XPS Spectra for 1.71 wt.% Cu-Doped TiO_2 (a) Survey; (b) Ti 2p; (d) Cu 2p and O1s Peak

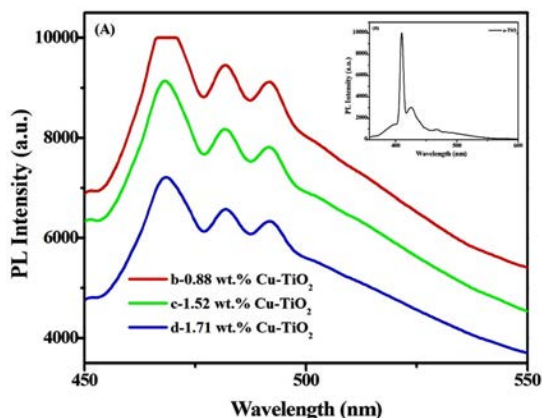


Fig. 6A: PL spectra of (b) 0.88, (c) 1.52 and (d) 1.71 wt.% Cu-Doped TiO_2 NPs and (B) Inset Fig. Shows (a) TiO_2

$$\text{Percentage Degradation} = \left[\frac{(A_0 - A_t)}{A_0} \right] \times 100 \quad (3)$$

Where, A_t is the absorbance after time 't' and A_0 is absorbance of dye solution before degradation. (Fig. 7) shows the photocatalytic activity of pure TiO_2 and Cu-doped TiO_2 samples under A) UV light B) Visible light and C) Direct sunlight. It is observed that the pure TiO_2 sample is more efficient than the Cu^{2+} doped samples in UV light irradiation. In contrast, under direct sunlight, the percentage degradation increases with increase in Cu^{2+} concentration. The important aspect of this work is that the degradation response of MG dye of synthesized catalyst is quick to the exposure to direct daylight. Hence it can be further used to study the degradation activities of various dyes in the industry for better color combinations. The degradation efficiencies were

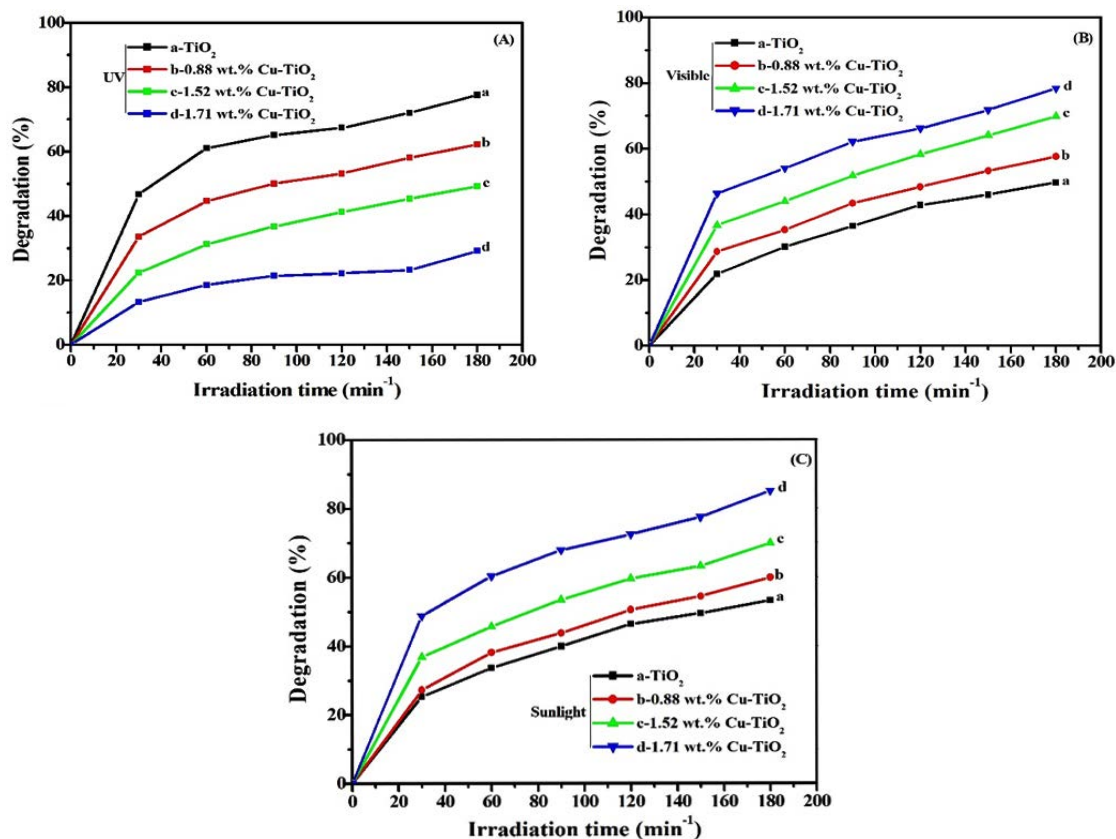


Fig. 7: Photocatalytic Activity of (a) TiO_2 , (b) 0.88, (c) 1.52 and (d) 1.71 wt.% Cu-Doped TiO_2 Under (A) UV Light, (B) Visible Light and (C) Sunlight for Degradation of Malachite Green Dye

calculated for UV, visible and direct sunlight and the samples were characterized by using various techniques.

To affirm the degradation of MG, the chemical oxygen demand (COD) is a consumption of oxygen present in water during the oxidation of inorganic compound and decomposition of organic content was resolved at various times, which is appeared in Table 4. Estimations at time interims of debasement process demonstrated a fall in the COD qualities, which additionally affirms the improved photodegradation of MG utilizing the Cu^{2+} doped TiO_2 catalysts. The fall in COD qualities demonstrated the comparable pattern as that seen by UV-visible spectrometer utilizing TiO_2 following 3 hours UV light illumination, the most extreme COD expulsion rate was 77.58 %. The COD expulsion rate was watched at least for TiO_2 following 3 hours of visible light illumination. The same expanded for COD exhaustion under visible light 57.58%, 69.87% and 78.32% for 0.88-1.71 wt.% Cu-doped TiO_2 nanoparticles. The comparative pattern was watched for COD consumption under direct daylight 59.88%, 69.88% and 85.10 for 0.88-1.71 wt.% Cu^{2+} doped TiO_2 nanoparticles. The observations obviously show higher photocatalytic movement can be gotten even with low measure of Cu^{2+} doped TiO_2 . The uppermost fall in COD was seen in 1.71 wt.% Cu-doped TiO_2 under direct daylight. By and large, under UV light the COD evacuation effectiveness diminishes with increment in Cu^{2+} doping attentiveness. While the COD evacuation effectiveness of Cu-doped TiO_2 increments with increment in the doping grouping of Cu^{2+} under visible and direct daylight.

Conclusions

Among the varied strategies, efficient and easy hydrothermal technique is employed for the

synthesis of nanosized TiO_2 and Cu-doped TiO_2 NPs. The key focus of the work is targeting on assess photocatalytic activity photodegradation of MG color. X-ray designs were researched the substitutional doping of Cu^{2+} into the TiO_2 lattices. The vitality bandgap is tuned into the visible region from 3.18 to 2.34 eV with an expansion in Cu^{2+} content in TiO_2 NPs. A more grounded actinic radiation absorption demonstrating the abatement inside the band gap while doping. The more drawn out wavelength absorption is designated to the development of polluting influence levels at interims the band gap of TiO_2 . TiO_2 displays unadulterated anatase segment and accordingly the particles achieve non-round and grouped uneven frame when doping of Cu^{2+} . XPS results uncovered that Cu was effectively joined into the TiO_2 grid. The least PL power was watched for ideal Cu^{2+} (1.71 wt.%) content because of more partition of the electron and hole pairs. The most elevated 85% photocatalytic degradation was seen inside 180 min under visible light for 1.71 wt.% Cu-doped TiO_2 nanoparticles contrasted with unadulterated TiO_2 . Molecule size diminishes with expanding Cu^{2+} content, the synergistic impact of Cu^{2+} doping and broadened the lifetime of a photogenerated e^- - h^+ pair were in charge of the change in photocatalytic action. The amount of photocatalytic degradation of the dye has also been studied by COD measurement.

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Conflict of Interest

The author(s) declare(s) that there is no conflict of interests regarding the publication of this article.

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